1/4
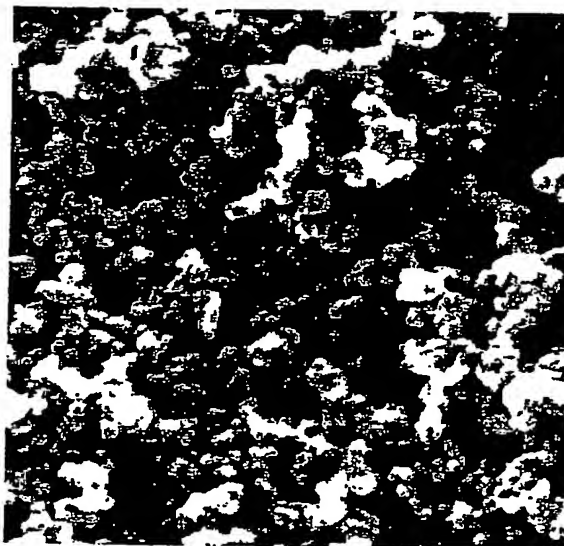
(54) MATERIAU CATALYSEUR AU CHELATE, EXEMPT DE PLATINE, POUR REDUCTION SELECTIVE PAR L'OXYGENE, ET SON PROCEDE DE FABRICATION

(54) PLATINUM-FREE CHELATE-CATALYST MATERIAL FOR THE SELECTIVE REDUCTION OF OXYGEN AND METHOD OF ITS PRODUCTION

(57)
Platinum-free chelate-catalyst materials for the selective reduction of oxygen have application in hydrogen and methanol fuel cells. Conventional catalyst material comprises an unsupported transition metal and a nitrogen- and a carbon-donor, which are polymerised to give a carbon matrix under pyrolytic conditions, in which the unsupported transition metal, functioning as electron donor and a nitrogen-coordinated transition metal chelate are bonded. The achievable porosity, catalytic activity and stability are however not adequate for commercial applications. Said chelate catalyst material comprises, in addition to the at least one unsupported transition metal, a nitrogen- containing organometallic transition complex, with a further transition metal different to the said transition metal and a chalcogenic component. The advantages of various transition metals and the chalcogens as electrically- conducting bridge formers can thus be combined. The unsupported transition metal in the form of a salt serves as filler during the formation of the carbon matrix, such that the above is embodied as an ultra-highly-porous material due to a foaming effect on thermal decomposition of said salt. Said chelate-catalyst material is particularly suitable for application in commercial industry, for example the auto-industry as a result of the high activity, stability and low cost thereof.

←――――→
200 nm

(54) Titre : MATERIAU CATALYSEUR AU CHELATE, EXEMPT DE PLATINE, POUR REDUCTION SELECTIVE PAR L'OXYGENE, ET SON PROCEDE DE FABRICATION
(54) Title: PLATINUM-FREE CHELATE-CATALYST MATERIAL FOR THE SELECTIVE REDUCTION OF OXYGEN AND METHOD OF ITS PRODUCTION
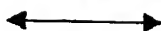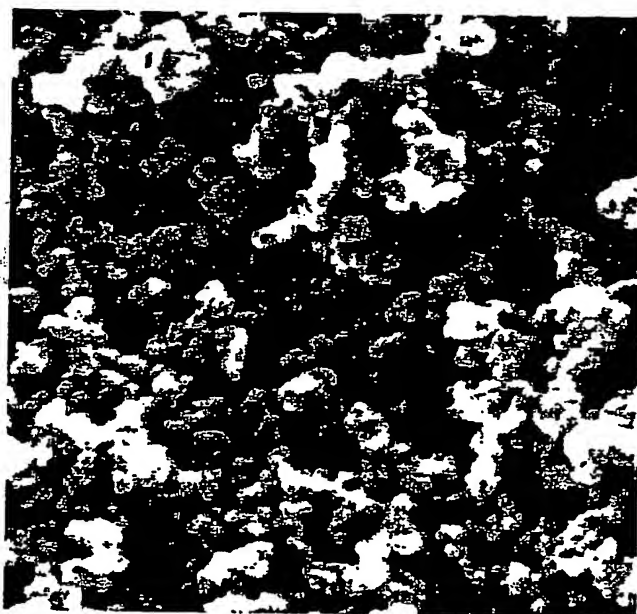
200 nm

(57) Abrégé/Abstract:
Platinum-free chelate-catalyst materials for the selective reduction of oxygen have application in hydrogen and methanol fuel cells. Conventional catalyst material comprises an unsupported transition metal and a nitrogen- and a carbon-donor, which are polymerised to give a carbon matrix under pyrolytic conditions, in which the unsupported transition metal, functioning as electron

(57) Abrégé(suite)/Abstract(continued):
donor and a nitrogen-coordinated transition metal chelate are bonded. The achievable porosity, catalytic activity and stability are however not adequate for commercial applications. Said chelate catalyst material comprises, in addition to the at least one unsupported transition metal, a nitrogen-containing organometallic transition complex, with a further transition metal different to the said transition metal and a chalcogenic component. The advantages of various transition metals and the chalcogens as electrically-conducting bridge formers can thus be combined. The unsupported transition metal in the form of a salt serves as filler during the formation of the carbon matrix, such that the above is embodied as an ultra-highly-porous material due to a foaming effect on thermal decomposition of said salt. Said chelate-catalyst material is particularly suitable for application in commercial industry, for example the auto-industry as a result of the high activity, stability and low cost thereof.

-2-

Abstract

Platinum-free chelate catalyst materials for the selective reduction of oxygen have application in hydrogen and methanol fuel cells. Conventional catalyst material comprises an unsupported transition metal and a nitrogen- and a carbon-donor, which are polymerized to give a carbon matrix under pyrolytic conditions, in which the unsupported transition metal, functioning as electron donor and a nitrogen-coordinated transition metal chelate are bonded. The achievable porosity, catalytic activity, and stability are, however, not adequate for commercial applications. Said chelate catalyst material comprises, in addition to the at least one unsupported transition metal, a nitrogen-containing organo-metallic transition complex, with a further transition metal different from the said transition metal and a chalcogenic component. The advantages of various transition metals and the chalcogens as electrically conducting bridge-formers can thus be combined. The unsupported transition metal in the form of a salt serves as filler during the formation of the carbon matrix, such that the above is embodied as an ultra-highly-porous material due to a foaming effect on thermal decomposition of said salt. Said chelate-catalyst material is particularly suitable for application in commercial industry, for example the auto-industry as a result of the high activity, stability and low cost thereof.

Platinum-Free Chelate Catalyst Material for the Selective
Reduction of Oxygen and Method of Its Production

Specification

The invention relates to a platinum-free chelate catalyst material for the
selective reduction of oxygen with at least one unsupported transition metal, a
nitrogen and a carbon component structured as a porous conductive carbon
matrix into which the unsupported transition metal and a transition metal
chelate coordinated by the nitrogen are respectively bonded as electron
donor and catalytic center, and to a method of its production.

A major field of application of catalysts are electrochemical cells and,
in this context, emission-free fuel cells in particular, for generating electricity
efficiently and in an environmentally friendly manner by converting the
chemical energy of a fuel oxidation reaction into electrical energy without prior
heat generation. The fuel cell is particularly efficient if hydrogen is converted
to electrical energy. From among the many types of fuel cells, the polymer
electrolyte membrane (PEM) which is suitable in an excellent manner for
operation with hydrogen / oxygen or hydrogen / air is to be specially
mentioned. In this connection, the low energy density of hydrogen is a
problem, however, which is the reason for the increasing use of methyl
alcohol as a fuel. On the one hand, methyl alcohol can be catalytically
converted into hydrogen and carbon dioxide in a vehicle (indirect methyl
alcohol fuel cell) or, on the other hand, it can be directly oxidized at the
anode. In this context, the one which can be realized in the technically
simplest way is the direct methanol / air fuel cell (DMFC). For that reason, it
may be considered to be a highly promising electrochemical source of energy

for small appliances and electric motors. Hitherto, mixed platinum / ruthenium sponges or s-called "carrier catalysts" have primarily been used as catalyst materials for the anode in DMFC's, in which minute metal particles are precipitated on a conductive carrier material such as carbon black or graphite. Pure platinum or supported platinum are used as catalyst for the cathode. However, pure platinum does not act selectively, and problems arise, therefore, if methane is used as the fuel. While the cathode and the anode are separated from each other by a proton-conductive membrane as a connector between them, but it is pervious to methane which may reach the cathode where it will be oxidized as well. In this manner, the cathode which is to reduce the air oxygen, depolarized and reduced conduction will occur.

The present invention resides in the field of platinum-free catalyst materials which reduce selectively and which are thus resistant to alkanoles, and, in this context, within the group of chelate catalyst materials. A chelate is a catalytically very active higher order complex compound in which a central metal ion, forming several compounds, is surrounded in the manner of a ring by one or more molecules or ions. Different platinum-free, methanol-resistant chelate catalyst materials in supported or unsupported form have already been described in scientific literature. Yet none of the known types of catalyst material hereinafter to be described have been technically used as their catalytic activity and stability cannot be judged to be sufficient. The presence of highly conductive carbon of a large specific surface is essential for technical applications. Not only does the high-temperature reaction of the chelates result in improved activity but it also increases the stability of the catalyst material. In this connection it is necessary to distinguish between direct feeding of conductive carbon, such as, for instance, carbon black, and an in-situ-production of the carbon matrix by the polymerization of suitable oregano-metallic chelates to which the invention relates also.

The article [I] "direct methanol - air fuel cells for road transportation" (B.D. McNicol et al., Journal of Power Sources 83 (1999) pp. 15-31, describes catalyst materials with non-noble metals for use in DMFC (Chapter 4.5.2).

Alternative preparations of organo-metallic chelates such as iron or cobalt porphyries and phtalo cyanines as well as tetraazaannulene are being described. In this connection, in a metal tetra phenyl porphyrene as the active chelate, a metal ion is surrounded by four nitrogen atoms (MeN_4) each of which is bonded to a monopyrrol ring. The catalytic activity of these compounds for oxygen reduction has also been known for some time. Different transition metals used in the chelates lead to different results. Whereas the use of cobalt leads to a significantly increased activity, iron results in a marked increase in the stability. Even if some of the reports relate to a very good catalytic activity, these materials nevertheless do not at present display sufficient stability to be useful in fuel cells.

The prior publication [II] by Contamin et al. reports upon the preparation of a cobalt-containing electrocatalyst by pyrolysis of cobalt tetraazaannulene in the presence of active charcoal soot (see O. Contamin, C. Debiemme-Chouvy, M. Savy and G. Scarbeck: "Oxygen electroreduction catalysis: Effect of Sulfur Addition on Cobalt Tetraazaannulene Precursors", Electrochimica Acta 45 (1999), pp. 721-729. When adding thio urea to the starter preparation, the authors observed a significant increase in the activity of the catalyst. The active center consists of two oppositely positioned cobalt atoms bonded to the carbon matrix by C-S-bridges.

JP 59138066 describes the production of a catalyst material by mixing transition metal compounds with cobalt, copper, nickel, molybdenum, and/or tin with iron, urea and, fo instance, a pyromellitinic acid anhydride followed by a temperature treatment in the presence of a conductive carbon substrate. It results in a metal-phtalo-cyanine-polymer with an integration of the used different transition metals which are bonded as cores into the metal chelates. The material is being proposed for use in alkaline fuel cells. As regards the parallel use of several different transition metals, a scientific paper is yet to be mentioned, which reports on the catalytic activity of unsupported mixtures of cobalt tetraphenylporphyrine (CoTPP) and iron tetraphenylporphyrene

(FeTPP). In accordance with the publication [III] by R. Jiang and D. Chu ("Remarkably Active Catalysts for the Electroreduction of O_2 to H_2O for Use in an Acidic Electrolyte Containing Concentrated Methanol", Journal of the Electrochemical Society 147 (12), pp. 4605-4609 (2000)), the binary mixture of CoTPP and FeTPP treated at 600°C under argon displayed an increased catalytic activity relative to pure temperature-treated substances. The structure of the material is, however, relatively compact and has no significant porosity.

U.S. Patent 6,245,707 describes methanol-tolerant electrocatalysts for the oxygen reduction on the basis of nitrogen-chelates with at least two different transition metals (e.g. metal tetraphenylporphyrene), which in the presence of a carbon support are converted by thermal treatment to an active cathode catalyst for use in low temperature fuel cells.

Mixing of a ferrous salt (iron acetate) with perylenetetracarboxyanhydride (PTCDA) followed by temperature treatment in the presence of ammonia (NH_3) gas for producing a chelate catalyst material is known from the essay [IV] "Oxygen reduction catalysts for polymer electrolyte fuel cells from the pyrolysis of Fe^{II} acetate adsorbed on 3,4,9,10 perylenetetracarboxylic dianhydride" by G. Faubert et al. (Electrochimica Acta 44 (1999), pp. 2589-2603). The PTCDA produces a porous conductive carbon matrix, and NH_3 introduces nitrogen. In the introduction of this essay particular attention is directed to the fact that for producing a stable non-noble metal-based catalyst material a transition metal such as Fe or Co derived from a salt, as well as a nitrogen and a carbon source, are required. This may be realized in situ by polymerization of the carbon source.

The prior art from which the invention is proceeding is described in the essay [V] "O_2 Reduction in PEM Fuel Cells: Activity and Active Site Structural Information for Catalysts Obtained by Pyrolysis at High Temperature of Fe Precursors" by M. Lefèvre et al. (J. Phys. Chem. B (2000)). In this context, Fe^{II} acetate as precursor compound is mixed with PTCDA as organic

compound in the presence of NH_3 as nitrogen precursor compound and is pyrolyzed at a high temperature in excess of 800°C. The polymerization of the metal and nitrogen-free PTCDA results in situ in a porous conductive carbon matrix into which individual iron atoms are adsorptively bonded as electron donors and as iron chelate coordinated by four nitrogen atoms. The essay reveals that the catalyst activity of the chelate catalyst material may be affected by way of the iron content and the temperature of the pyrolysis. However, this is insufficient for any commercial application which is based not least on the relatively low attained porosity. Furthermore, no adequate stability can be attained. Moreover, in the synthesis, a matrix former as well as a nitrogen donor separated therefrom, must be used in addition to the transition metal.

It is, therefore, an object of the invention to provide a platinum-free chelate catalyst material of the kind referred to above, which is of a particularly high catalytic activity and stability and which is thus particularly suitable for commercial applications. In this connection, the knowledge gained form the prior art in respect of the effects of different transition metals and the obtainable porosity is to be taken into consideration. In addition, the chelate catalyst material in accordance with the invention is to consist of few components and is to be producible by but a few manufacturing steps even on a large industrial scale.

In connection with the chelate catalyst material in accordance with the invention with at least one unsupported transition metal as well as a nitrogen and a carbon component, the method is accomplished by the nitrogen and carbon component being formed as a common nitrogen-containing organo-metallic transition complex with a further transition metal different from the unsupported transition metal with the further transition metal being coordinated with the transition metal chelate by the nitrogen and by a chalcogen compound is bonded into the carbon matrix between the unsupported transition metal sporadically occurring in the carbon matrix and

the coordinated transition metal chelate.

In accordance with the chelate catalyst material in accordance with the invention, a carbon matrix structured into the nanometer range is formed by polymerization from the nitrogen-containing organo-metallic transition complex. As a result of free ions of at least two transition metals, the carbon matrix, as well as being electrically conductive, is also permeated by catalytic reaction centers. The bonded unsupported transition metal ions act primarily as electron donors for the reaction centers which consist of the further transition metal in the nitrogen-containing organo-metallic transition complex and which are coordinated by the nitrogen atoms into active Me-N_4-cores. By a combination of different transition metals in the chelate catalyst material in accordance with the invention, the advantageous properties thereof may additively be exploited in various functions. On the one hand, the catalytic activity and on the other hand the stability may be significantly increased by an appropriate selection of the transition metals which are respectively bonded into the carbon matrix as electron donors and chelate cores. The additionally provided chalcogen component contributes to a further increase of the catalytic activity in the inventive chelate catalyst material. The unsupported and the coordinated transition metal are electrically connected to each other by integrated chalcogen bridges so that the electrons from the electron donating transition metal may be transmitted particularly well to the catalytically active transition metal in the chelate cores.

In the chelate catalyst material in accordance with the invention only a small portion of the unsupported transition metal derived during synthesis from the used precursor compound is bonded to the carbon matrix. By far the largest portion serves during in-situ production of the carbon matrix as a nano-pore forming filler material and following their formation are washed out again (see below) in a separate step of the method. In this aspect, the catalyst material differs from the electro catalysts described supra. The additional space-maintaining function of the unsupported transition metal

yields a highly porous structuring of the carbon matrix which by enlargement of the active surface also contributes to an increase in the catalysis activity. Thus, the unsupported transition metal which is present as a metal oxalate for instance, acts as a blowing agent during the polymerization of the nitrogen-containing transition metal chelate. Moreover, the chelate catalyst material in accordance with the invention is compounded of a few components only since the nitrogen and the carbon donor are combined in a common material component.

The platinum-free chelate catalyst material described in the context of the invention may be used in the cathode of a fuel cell. The costs of the material amount at most to one tenth of the costs of a platinum-containing catalyst material. Hence, utilization of the material in accordance with the invention contributes to a significant lowering of the costs of a fuel cell module of conventional construction which continues to utilize the platinum-containing catalyst materials. Further advantages of the inventive chelate catalyst material are its unlimited availability of the components used and its alconal resistance, so that permeation of methanol to the cathode does not result in a reduced efficiency of the fuel cell.

Further improvements will be apparent from embodiments of the chelate catalyst material in accordance with the sub-claims. In detail, this may relate to at least one unsupported transition metal being a group VIII transition metal, in particular iron or ruthenium. The elements of this group exhibit an especially high catalytic effectiveness; often they are used as finely dispersed particles. Their presence not only affects a physical deposit of the reacting substances on the surface (adsorption), but also a chemical activation of the adsorbed particles. The activity of ruthenium especially resembles that of platinum without, however, reaching the level of costs thereof. It represents a highly promising alternative to platinum. While the raw material costs of ruthenium as a noble metal exceed those of simple transition metals and is of lower specific catalytic activity. However, by an

appropriate treatment its catalytic activity may be significantly increased. It is possible to combine several transition metals. The improvements of the effects may be achieved by ion formation as well as by the formation of nanoparticles from the chosen transition metals. Ruthenium in particular, when used as unsupported transition metal, can form particularly small nano-particles which in turn result in an ultra-highly porous carbon matrix. In addition, ruthenium constitutes an excellent electron donor. Its application thus results in an increase of the catalytic activity as well as of the stability.

The further transition metal different from the unsupported transition metal in the nitrogen-containing organo-metallic transition complex may, in accordance with a further embodiment of the invention, be cobalt or iron, in particular. In a combination of iron as the unsupported transition metal and cobalt as the transition metal in the nitrogen-containing organo-metallic transition complex their advantages may be optimally used in aa catalysis. Iron, the positive effects of which have already been described in detail above, is an excellent electron donor. It also increases the stability; cobalt, on the other hand, improves the activity of the catalyst material. Advantageously, the nitrogen-containing organo-metallic transition complex is a metallo-porphyrine. It may contain cobalt or iron and may, more particularly, be constituted as cobalt tetramethoxyphenylporphyrine or iron tetramethoxyphenylporphyrine. Metalloporphyrines exhibit an excellent catalytic ability because the active transition metals are freely coordinated in space by four nitrogen bonds. As a result, both surface accessibility and catalytic effect are optimal. In combination with the respective other transition metal as the unsupported transition metal the effects are improved still further. In the metalloporphyrine both or more transition metals may be applied. The metalloporphyrine combines the nitrogen and the carbon donor with each other. In highly cross-linked structures, it polymerizes already at moderate process temperatures in the range of 450° C and during in situ synthesis it is forming an ultra highly porous yet stable carbon matrix. The in situ production results in a particularly homogeneous distribution of the

electron donors and of the active cores within the carbon matrix. This ensures a uniformly high quality of the inventive chelate catalyst material. To augment the carbon matrix an added carbon support, particularly carbon black, may be provided. For instance, an electron-donating transition metal may be supported by carbon and may thus facilitate and improve the production of the carbon matrix by adsorptive bonding.

The positive effects of transition metals on the electro-chemical catalysis are well known. But the organic chalcogen compound additionally utilized in the chelate catalyst material in accordance with the invention has a significant effect on the catalytic activity, particularly as regards a catalytic initial action. In this connection, it may be advantageous to add the chalcogen in elementary form (e.g. sulfur) or as an organic chalcogen compound (e.g. thio urea). The positive effects of sulfur, in particular for forming bridges, are generally known. Its lower toxicity and greater availability, compared to selenium, are also known. For that reason, the chalcogen compound in accordance with a further embodiment of the invention, may be sulfur urea which may be synthesized in a simple manner and which may be used for many purposes. Urea ($OC(NH_2)_2$) as well as carbamide also contain nitrogen. Thus, the further advantage results of an additional nitrogen donor being available for the coordination during chelate formation in the catalyst material in accordance with the invention.

A particularly simple and process-efficient method of producing a platinum-free chelate catalyst material for the selective reduction of oxygen with at least one unsupported transition metal, a nitrogen and a carbon component structured as a porous conductive carbon matrix into which are bonded the unsupported transition metal as an electron donor and transition metal coordinated by the nitrogen as a catalysis center, provides for the following method steps:

♦ mixing of a transition metal salt as precursor compound for the unsupported transition metal with the nitrogen-containing organo-

metallic transition complex and the organic chalcogen compound;

♦ heating the mixture to a pyrolysis temperature in the range of 450° C during a period of a several hours;

♦ cooling the polymerized mixture and mixing with an acid;

♦ boiling the acid mixture during a period of a few minutes and subsequent cooling;

♦ removal of the resultant powder by suction and washing with deionized water;

♦ drying of the powdered chelate catalyst material.

During production of the chelate catalyst material in accordance with the invention, a spongy transition metal containing carbon matrix is formed by a fine transition metal salt being initially covered with the nitrogen-containing organo-metallic transition complex and the organic chalcogen compound by mixing. The mixture is then subjected to pyrolysis at a moderate temperature range of 450° C. This initially causes evaporation of the crystal water gebunden in the transition metal salt. Thereafter, the organic chalcogen compound decomposes, and the nitrogen-containing organo-metallic transition complex melts. The latter begins to polymerize causing a strongly cross-linked and, hence, very stable carbon matrix to be formed. During this process, decomposition of the at least one unsupported transition metal salt commences simultaneously. This causes formation, with the generation of a gas, of nanocrystals from the unsupported transition metal. However, a fraction of the transition metal is also firmly bonded to the carbon matrix. The carbon matrix formed from the polymerizing nitrogen-containing organo-metallic transition complex deposits around the nanocrystals from the at least one transition metal. At the selected moderate process temperature, the coordination sphere for the MeN_4 cores is substantially maintained. The chalcogen from the organic chalcogen compound is bonded into the carbon matrix as electrically conductive connecting bridges between the unsupported transition metal and the chelate cores. The formed nanocrystals are then are then washed out in a subsequent step which is entirely novel in the context of

such methods of synthesis, and a conductive highly porous carbon matrix with nano and micro structures and containing transition metals, chalcogen and nitrogen remains.

The formed highly porous carbon matrix is already of excellent stability and activity for the selective oxygen reduction. However, in accordance with a particularly advantageous embodiment of the method, the activity can be further improved by a process step to be executed before or after the process step of boiling the acid mixture:

♦ Heating the powdered chelate catalyst material under a protective atmosphere to a high temperature in the range of 850° C over a period of one hour or more.

Furthermore, iron may be provided as unsupported transition metal by iron oxolate as a precursor material. Oxalate is the salt of oxal acid; it is very reactive and is available at low cost on an industrial scale.

By explanation of an embodiment and by drawings, the advantageous activity of the chelate catalyst material in accordance with the invention is to be explained in still greater detail. In the drawings:

Fig. 1 is a thermogravimetric decomposition curve of the unsupported metal (iron oxalate) in the presence of the platinum-free chelate catalyst material;

Fig. 2 is an image taken with a raster electron microscope of the platinum-free chelate catalyst material after termination of its preparation;

Fig. 3 is an EXAFS spectrum inn the presence of the platinum-free chelate catalyst material; and

Fig. 4 is a current density diagram of the platinum-free chelate catalyst material compared to a standard platinum catalyst.

Embodiment

3.35g of iron oxalate $FeC_2O_4 \cdot 2H_2O$ as precursor compound is mixed with .65 g of cobalt tetramethoxyphenylporphyrine (CoTMPP) as nitrogen-containing metal-organic transition complex and .18 g of sulfur urea as organic chalcogen compound and heated to 450° C for 2 h and then at 850° C for 1 h. The mixture is cooled and suspended with 300 ml of 1N HCl solution under an argon atmosphere and thereafter heating to boiling for 30 min. After cooling, the black powder is removed on the filtration device by suction and washed in deionized water. Thereafter, is powder is dried.

In the embodiment, a spongy iron-containing carbon matrix is formed by covering a fine iron oxalate with CoTMPP and sulfur urea. This mixture of iron oxalate, CoTMPP and sulfur urea is then subjected to temperature treatment. Initially, the crystal water gebunden in the iron oxalate evaporates. Thereafter, the sulfur urea decomposes. The CoTMPP melts and begins to polymerize causing formation of a carbon matrix. In this connection, see Fig. 1, which depicts thermogravimetric curve (loss of mass TG, solid line) of the two—stage decomposition of cobalt tetramethoxyphenylporpyrine (CoTMPP) in the presence of iron oxalate. In a first stage, crystal water of the iron oxalate is evaporated, shown by the simultaneously measured mass signal $m/e = 18$ (dashed line in the upper diagram). In a second stage, the iron oxalate decomposes ($m/e = 44$, CO_2 formation, dotted line in the upper diagram) as well as, during the same temperature interval, the CoTMPP, shown by the mass $m/e = m78$ (C_5H_6 formation, dot-dashed line in the lower diagram).

The decomposition of the iron oxalate commences at the same time as the polymerization process. This leads, with a simultaneous development of CO_2 and CO gas, to the formation of iron[II] oxide (FeO) nanocrystals; but a fraction of the iron will also be firmly bonded into the carbon structure. The carbon matrix formed from the polymerizing CoTMPP deposits around these nanocrystals. At the temperature at which these processes are conducted the coordination sphere of the cobalt ions is substantially maintained. The

sulfur released from the sulfur urea is integrated as an electrically conductive connection bridge into the carbon matrix between the electron-donating iron and the catalytically active cobalt chelate. The nitrogen atoms also released during the decomposition are used in the coordination of the cobalt atoms relative to the chelate chores in addition to the nitrogen atoms from the CoTMPP. The formed FeO crystals are then washed out during an ensuing step and a conductive, highly porous iron, cobalt nitrogen and sulfur-containing carbon matrix remains. The activity of this substrate as regards oxygen reduction is already very good. The activity can, however, only be further increased by a further temperature treatment at 850° C.

In order to judge the porosity of the catalytic materials, the specific capacity of the catalyst material in accordance with the invention was defined by electro-chemical experiments under nitrogen. Capacities between 100 and 300 F/g were attained. The values are in the range of commercial highly porous carbon black. Moreover, investigations with a raster electron microscope confirmed the high porosity of the material up into the range of nanometers. In this connection, see Fig. 2, which depicts an image of the catalyst material in accordance with the invention formed with a raster electron microscope following acid treatment. The highly porous structure may be clearly seen.

In research relating to catalysts it is considered to be firmly established that transition elements are acting catalytically since in their absence no chemical changes take place. Also, the existence of the electron and its inevitable participation in chemical reactions is scientifically undisputed. By extended X-ray absorption fine structure (EXAFS) analysis and using synchrotron radiation it was possible to measure the spacing between the transition metals and the elements nitrogen, carbon and oxygen in catalyst material in accordance with the invention. In this connection, see Fig. 3, which depicts Fournier-transformed EXAFS spectra at the Fe and Co edge of a carbon- supported Fe-Co catalyst which was produced by pyrolysis of

CoTMPP in the presence of iron oxalate. To remove pure metal particles the catalyst was etched in acid prior to being measured. The peak layers detected allow an inference of the presence of metal-nitrogen bonds (nitrides) in the catalyst material, in addition to the metal carbon (carbide) and metal oxygen (oxides), which are considered cores of previous nitrogen coordinated transition metal chelates in an __in situ__ formed carbon support.

Electrochemical Characterization

10 mg of the chelate catalyst powder are suspended for 30 min in a ultra-sound bath in a mixture of 1 ml of an ethanolic .2% NAFION solution and 1 ml of deionized water. 5 ml of this suspension are deposited by a dropper on a polished glassy carbon electrode of 1 mm diameter and dried in air. The working electrode thus prepared is measured in a 3 electrode arrangement in O_2 saturated solution, with a mercury sulfate electrode as a reference electrode and a platinum wire as a counter electrode in .5 M H_2SO_4 solution as an electrolyte. The diffusion-corrected current densities as a function of the potential difference between working and counter electrode are shown in Fig. 4 by comparison to a standard platinum catalyst (20% platinum on Vulcan XC 72R of Etek Inc., upper curve.

The voltage differences relative to the Etek catalyst are

- 60 mV   at .2 mA/cm^2;
- 40 mV   at 2 mA/cm^2;
- 20 mV   at 10 mA/cm^2; and
- 0 mV   at 20 mA/cm^2.

The measured voltage differences drop at increasing current density and relative to the prior art are to be classified as extremely small. The platinum-free chelate catalyst material in accordance with the invention thus has a catalytic activity which is almost identical to a conventional standard catalyst material using expensive platinum.

Patent Claims:

1.   A platinum-free chelate catalyst material for the selective reduction of
     oxygen with at least one unsupported transition metal, a nitrogen and a
     carbon component structured as a porous conductive carbon matrix,
     into which the unsupported transition metal is bonded as an electron
     donor and a transition metal chelate coordinated by the nitrogen is
     bonded as a catalysis center,
     characterized by the fact that
     the nitrogen and the carbon component are commonly formed as a
     nitrogen-containing organo-metallic transition complex with a further
     transition metal different from the unsupported transition metal, the
     further transition metal being coordinated to the transition metal
     chelate by the nitrogen, and an organic chalcogen compound being
     also bonded into the carbon matrix as an electron-conductive bridge-
     former between the unsupported transition metal occurring but singly in
     the carbon matrix and the coordinated transition metal chelate.

2.   The platinum-free chelate catalyst material of claim 1,
      characterized by the fact that
      that the at least one unsupported transition metal is a group VIII
      transition metal,
      in particular iron or ruthenium.

3.   The platinum-free chelate catalyst material of claim 1 or 2,
      characterized by the fact that
      the further transition metal in the nitrogen-containing organo-metallic
      transition complex differing from the at least one unsupported transition
      metal is a group VIII transition metal, in particular cobalt or iron.

4.   The platinum-free chelate catalyst material of one of claims 1 to 3,
      characterized by the fact that
      the nitrogen-containing organo-metallic transition complex is a
      metalloporphyrine.

5.   The platinum-free catalyst material of claim 4,
      characterized by the fact that
      the metalloporphyrine contains cobalt or iron and is structured in
      particular as cobalt tetramethoxyphenylporphyrine (CoTMPP) or iron
      tetramethoxyphenylporphyrine (FeTMPP).

6.   The platinum-free chelate catalyst material of one of claims 1 to 5,
      characterized by the fact that
      it contains an additional carbon component, in particular carbon black,
      for augmenting the formation of the carbon matrix.

7.   The platinum-free chelate catalyst material of one of claims 1 to 6,
      characterized by the fact that
      the chalcogen in the organic chalcogen compound is sulfur.

8.   The platinum-free chelate catalyst material of claim 8,
       characterized by the fact that
       the organic chalcogen compound is sulfur urea.

9.   A method of producing a platinum-free chelate catalyst material for the
       selective reduction of oxygen with at least one unsupported transition
       metal, a nitrogen and a carbon component structured as a porous
       conductive carbon matrix into which the unsupported transition metal is
       bonded as an electron donor and a transition metal chelate
       coordinated by the nitrogen is bonded as a catalysis center in
       accordance with one of claims 1 to 8, with the method steps of:
   ♦   mixing of a transition metal salt as precursor compound for the
       unsupported transition metal with the nitrogen-containing organo-
       metallic transition complex and the organic chalcogen compound;
   ♦   heating the mixture to a pyrolysis temperature in the range of
            450° C during a
       period of several hours;
   ♦   cooling the polymerized mixture and mixing with an acid;
   ♦   boiling the acid mixture during a period of a few minutes and
       subsequent cooling;
   ♦   removal of the resultant powder by suction and washing with deionized
       water; and
   ♦   drying of the powdered chelate catalyst material.

10.   The method of producing a platinum-free chelate catalyst material of
       claim 9 with a further method step to be performed before or after the
       method step of boiling the acid mixture:
   ♦   eating the powdered chelate catalyst material under protective
       atmosphere to a high temperature in a range of 850° C during a period
       of one hour or more.

11. The method of producing a platinum-free chelate catalyst material of claim 9 or 0 with iron oxalate as a precursor compound for providing iron as unsupported transition metal.

17a

Application number / numéro de demande:___DE 02/02496___

Figures:___2.___

Pages:_____

Unscannable items
received with this application
(Request original documents in File Prep. Section on the 10ʰ floor)

Documents reçu avec cette demande ne pouvant être balayés
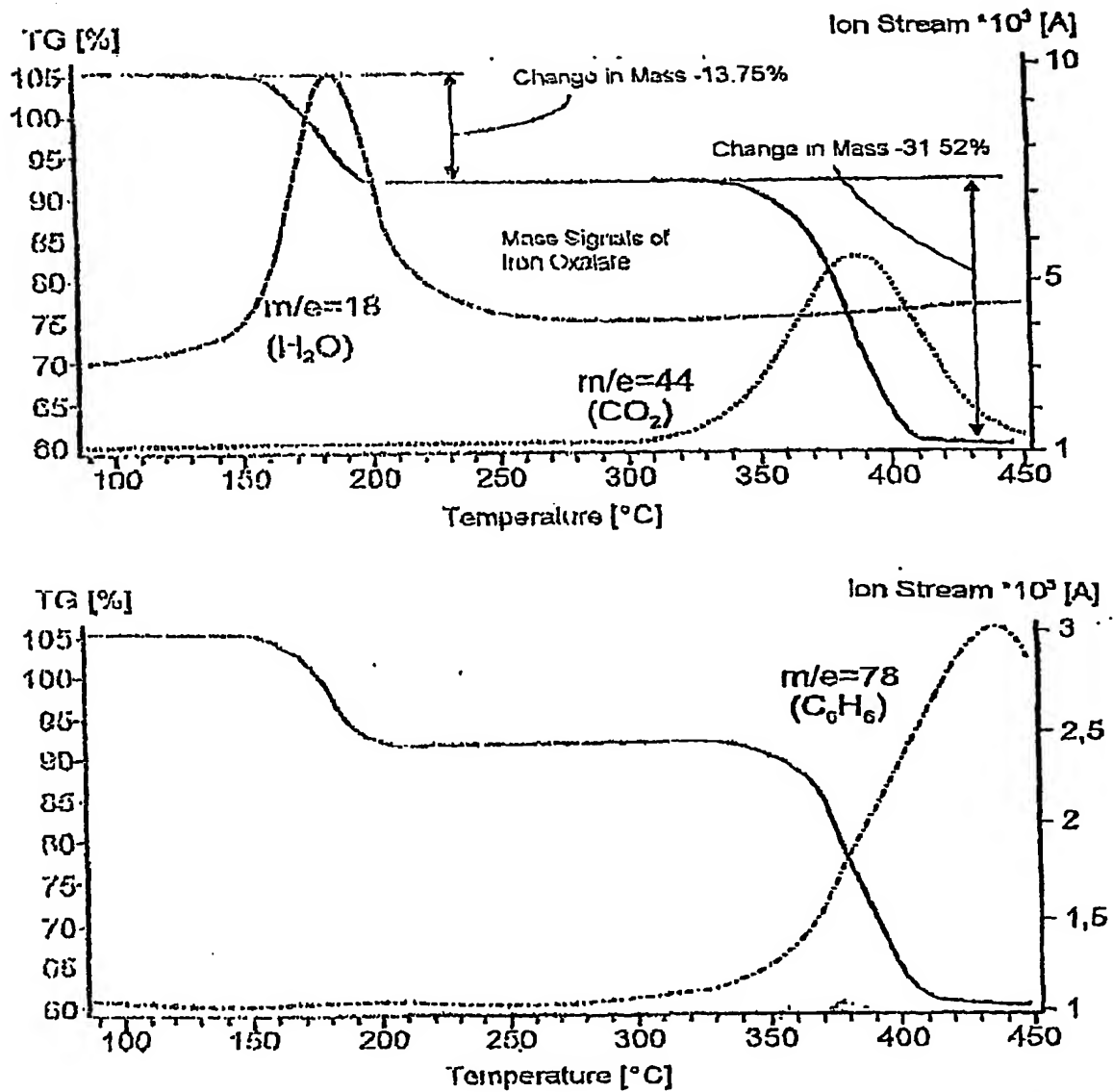(Commander les documents originaux dans la section de préparation des dossiers au
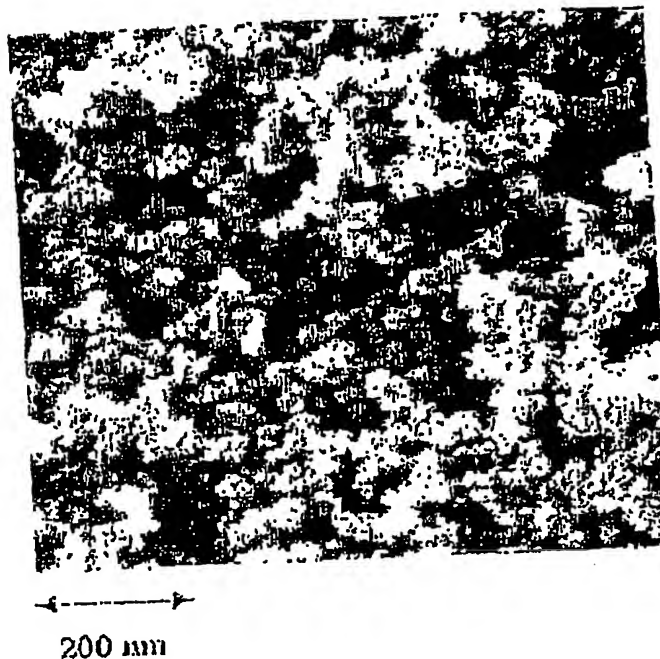10ème étage)

Fig.1

Fig.2

← - - - - →

200 mm
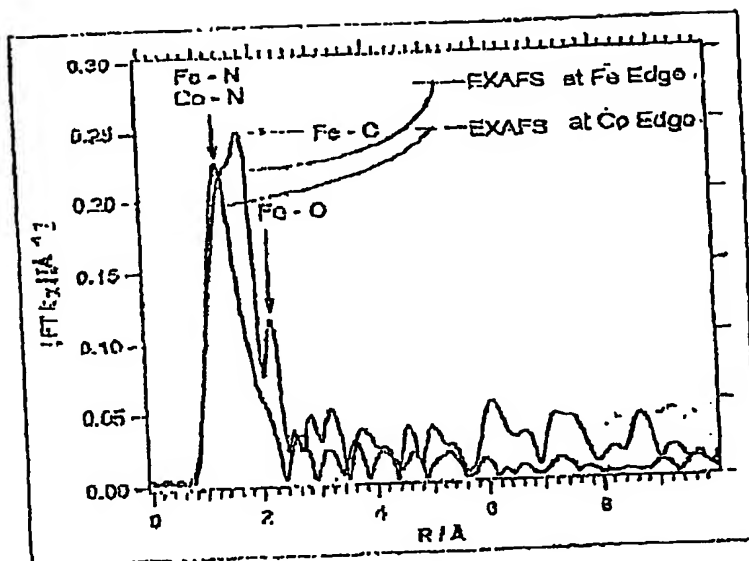
Fig.3
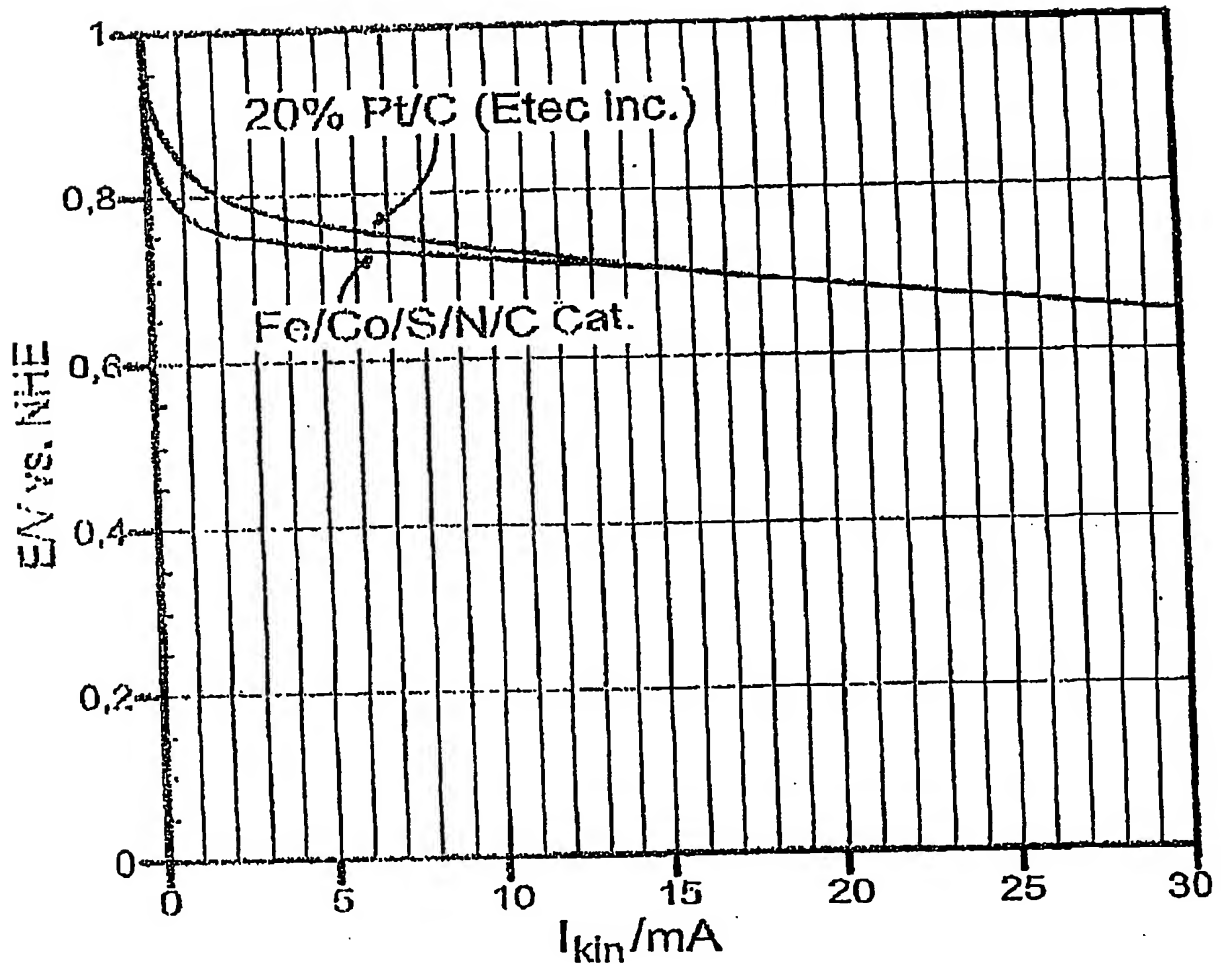
Fig.4
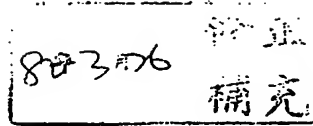
MCUS 1077

CATALYST MATERIAL DERIVED FROM PRECIOUS METAL-
CONTAINING MACROCYCLIC COMPOUND PRECURSORS, THE
METHOD FOR PREPARATION THEREOF AND THE METHOD
FOR ACTIVATING THE CARBON-SUPPORTED PRECIOUS METAL

This invention relates to an improved catalyst material, and in particular to a catalyst material of particular interest for fuel cells and

5   batteries.

In a fuel cell, a fuel, which may be hydrogen, a hydrocarbon or an oxygen-containing fuel such as methanol, is oxidised at a fuel electrode (anode), and oxygen is reduced at a cathode. An electrolyte,

10   which may be alkaline or acidic, and in liquid or solid state, contacts the electrodes, which may be coated with an electrocatalyst. There have been many proposals for such fuel cell electrocatalysts.

A phosphoric acid fuel cell (PAFC) operates with an electrolyte of concentrated phosphoric acid, typically at temperatures of between 180°C and 220°C. Any material used for the cathode or anode must be stable with respect to the temperature at which the fuel cell operates and maintain reasonable activity in the presence of the phosphoric acid.

A proton exchange membrane fuel cell (PEMFC) is another type of acidic electrolyte fuel cell, in which the electrolyte is a solid proton-conducting polymer. The PEMFC is typically operated at around 80°C to 100°C.

The PAFC is the type of fuel cell closest to commercialisation and there are a number of demonstration units, especially in Japan, where there are considerable economic and environmental pressures to reduce imports of hydrocarbon fuels and to cut polluting emissions from power generation. It is envisaged that the PAFC will find applications in the multi-megawatt utility power generation market and also as combined heat and power, ie co-generation, systems, in the 50 to several hundred kW range. The PEMFC can provide much higher power density output than the PAFC, and can operate efficiently at much lower temperatures. Because of this, demonstration units of this type of fuel cell are being built for evaluation in various applications. This is of particular interest in the United States, where continuing concern over polluting emissions from motor vehicles may restrict the use of combustion engines in the future.

Many people consider that these fuel cells are, however, unlikely to get beyond the demonstration stage because power output is

too low for the capital costs involved. In both the PAFC and the PEMFC, power output is limited in part by the activity and durability of the cathode catalyst. Increasing cathode catalyst activity and stability can result in higher, sustainable, power density at the same efficiency. The capital cost per unit of power is therefore reduced in proportion to the increase in performance. Because the cost of the cathode catalyst is a small fraction of the cost of the fuel cell stack, increasing the power density of the stack reduces the capital cost per unit power out of all proportion to the value of the catalyst per se. It is therefore widely recognised that a cathode catalyst with improved performance would have great value in reducing overall capital cost per unit power.

In addition to the need for improved catalyst activity, it is also vitally important that the electrodes containing these catalysts should maintain this high activity throughout the lifetime of the fuel cell, with ideally, no performance decay.

It has become accepted in the fuel cell catalyst art that a "standard" catalyst formulation for electrodes for fuel cells with acidic electrolytes, eg the PAFC and the PEMFC, comprises platinum, by itself or as an alloy, either as a high surface area black, ie metal powder, or supported on a high surface area conducting carbon substrate material. The most active catalysts are supported on high surface area conducting carbons, and are made by techniques involving complex platinum solution chemistry, many of which remain as proprietary processes. Mention can be made of the method disclosed by H Petrow and R Allen (USP 3,992,512), in which very small colloidal particles of platinum are adsorbed from solution onto the carbon support. Very small crystallites

of platinum, ranging from 15-30Å, are formed in the carbon, and these provide a catalyst with very high activity. Alloy catalysts of Pt, typically with metals from Group III to Group VIII of the Transition Metal series, are most commonly formed by adsorption of the base metal onto a preformed platinum on carbon catalyst, followed by heat at temperatures above 700°C to effect formation of the alloy. These materials possess higher activity than pure platinum catalysts and are the most active catalysts developed for use in acid electrolyte fuel cells such as the PAFC. Such alloy materials are disclosed in USP 4,447,506.

It is appropriate here to define the term activity. Activity is defined as the maximum current obtained from the catalyst, when fabricated into an electrode, at a given voltage (ie, efficiency) divided by the weight of active catalyst in the electrode. It is therefore also known as the "mass activity". When comparing different catalysts, an increase in activity is thus related to the current density increase for the same active catalyst metal content. There is good agreement in the prior art that when evaluated as oxygen reduction cathodes in 100% phosphoric acid at 180°C with pure oxygen as the reactant, the most active platinum supported on carbon catalysts have activities ranging from 30-40mAmg^{-1}Pt at 900mV vs SHE (Standard Hydrogen Electrode) (see for example P Ross, Precious Metals 1986, International Precious Metals Institute, Allentown, PA, 1986, p 355-363; L Keck et al, 1st International Fuel Cell Workshop, Tokyo, Sept 16th 1989, p 29-39; F Luczak, D Landsman, USP 4,447,506). On alloying, the activity of the most active Pt alloy catalysts are reported (also in the preceding references) to be in the range 50-60mAmg^{-1}Pt.

During practical fuel cell operation, the cells are operated at fixed current density output, and it is desirable to maintain as high and as stable a cell voltage as possible to maintain high efficiency and power output. For PAFC's the voltage performance of the cathode containing this platinum catalyst typically declines at a rate of from 1 to 10mV per 1,000 hours of operation. Part of the reason for this decline is due to sintering, wherein the active catalyst particles tend to coalesce, either by surface migration or dissolution/re-precipitation, causing a reduction in effective surface area and hence in activity. It is also possible that platinum can be permanently lost from the cathode by dissolution into the electrolyte. It has been reported (J Aragane, J Electrochemical Society, 135, 844, 1988) that, in an operation of a PAFC for 4,500 hours, 60% of the platinum content of the cathode was lost by dissolution. This loss in platinum electrocatalyst performance is one of the most serious technical problems encountered in fuel cells.

Increasing PAFC temperatures, pressures and potentials accelerates catalyst de-activating processes.

The development of active catalysts having good stability is therefore extremely desirable. Many attempts have been made.

Metal-containing macrocyclic compounds have been investigated for a number of years as fuel cell catalysts. These studies have almost exclusively centred on the use of base metal macrocyclic compounds. A macrocyclic compound is defined as a cyclic compound with nine or more members (including all heteroatoms) and three or more ligating atoms (Coordination chemistry of Macrocyclic Compounds, G A Melson, Plenum

Press, New York & London, 1979). Amongst the metal macrocyclic compounds are N4-chelate compounds, such as phthalocyanines, porphyrins and tetraazaannulenes.

5   Although some of these materials have found use as fuel cell cathodes in alkaline electrolytes, such as potassium hydroxide, their performance as regards activity and especially stability, has been unsuitable for use in the more widely employed acid electrolyte fuel cells. In fact there are no instances of this type of material having any practical use in

10   acid electrolyte fuel cells under the operating conditions of temperature and electrolyte concentration that are normally employed.

GB 2,164,785A discloses the use of transition metal phthalocyanine compounds as catalyst materials. The use of platinum

15   phthalocyanine as a cathode with 6M alkaline potassium hydroxide as electrolyte is described. Van Veen et al, (Electrochimica Acta, **24** 921-928, 1979), discusses activity for a number of macrocycles of Pt, Pd, Ru, Fe, Co, Mn and Zn with either H_2SO_4 or KOH as the electrolyte. Further disclosures by Van Veen et al, (Ber Bunsenges Phys Chem, **85**,

20   693-700, 1981; and J Chem Soc, Faraday Trans 1, **77**, 2827-2843, 1981) include activity measurements for a number of other macrocycles. One of the examples is iridium(III) meso-tetra(para-isopropylphenyl)porphyrin chloride which after heat treatment showed an oxygen reduction activity of $2.2mAmg^{-1}$ of catalyst, at 850mV, with an electrolyte of 4M H_2SO_4,

25   at 23°C. NL 8003387 also discloses a carbon supported iridium(III) meso-tetra-(para-isopropylphenyl)porphyrin chloride electrocatalytic material in which the activity for oxygen reduction is quoted as $2.0mAmg^{-1}$

catalyst at 850mV and after running at $1.0mAcm^{-2}$ for 16 hours a loss of 10mV occurred.

Yeager et al, (DOE Report October 1984 LBL-18542) have disclosed a μ-oxo-di(iron(III)meso-tetra(para-methoxyphenyl)porphyrin) catalyst material supported on a high surface area activated carbon, for use as a cathode with phosphoric acid as electrolyte. On evaluation with oxygen as the reductant, in 85% phosphoric acid, at 100°C, the activity at 900mV reached a maximum of $5.0mAmg^{-1}$ of iron. After operation of a cathode comprising this catalyst, at a temperature of only 100°C, at a current density of $100mAcm^{-2}$ for 7.5 hours, a performance decay of 60mV was reported. Although this performance is amongst the highest reported for a macrocyclic material in an acid electrolyte, the decay rate is still far too great to be of any use. Furthermore, it has been reported that this material was unstable at temperatures greater than 100°C, and as such would again have no application in a practical phosphoric acid fuel cell operating at a temperature above 180°C.

In all this prior art the actual catalysts are the macrocyclic compounds themselves, which can be characterised by the central metal atom species being in an oxidised form; ie a valence state greater than zero. Inert atmosphere heat treatments have been used on prior art materials in attempts to improve catalyst activity and durability. Such treatment has the apparent effect of partially degrading the macrocycle and forming a closer interaction between catalyst and support. While this does result in a more durable and (sometimes) a more active catalyst, even these catalysts do not show good activity and stability under phosphoric acid fuel cell conditions (Yeager, ref above). The materials are not subjected to an activation procedure to modify the chemical state of the

metal. This is discussed by K Wiesener et al   (Mater Chem Phys, **22**, 457, 1989).

We have invented a novel catalyst material which demonstrates higher activity for catalysing fuel cell reactions than all prior art materials, and also shows enhanced stability in acidic electrolytes compared to all prior art materials.

- .The novel catalyst material, supported on high surface area carbons, may be derived from precursors of precious metal-containing macrocyclic compounds.   Said precursors undergo an activation process, which modifies the chemical state of the catalytic metal, to produce the precious metal catalyst material.

Accordingly, the present invention provides a catalyst material derived from precious metal-containing macrocyclic compound precursors and supported on high surface area carbons, which catalyst material contains precious metal in zero oxidation state.

Preferably the precursor material undergoes an activation process to give the catalyst material containing precious metal in the zero oxidation state.

The invention also provides a fuel cell, having at least one electrode coated with the electrocatalytic material of the invention.

The invention further provides an electrode, coated with the catalytic material of the invention.

Suitable precious metals are the platinum group metals, Pt, Pd, Ru, Os, Rh, Ir, and gold and silver. Preferably the precious metal is platinum or iridium. The macrocycle may be an N4-chelate compound and is preferably a phthalocyanine, a porphyrin or a tetraazaanulene. Most preferably, the macrocycle is a phthalocyanine or tetraazaannulene.

Suitable carbon supports are of the type commercially available. They may be prepared specifically for this application. Preferred carbons are the highly conductive oil furnace blacks and acetylene blacks. The carbon supports may be predominantly amorphous or graphitic. They may be prepared commercially, or specifically treated to increase their graphitic nature. Particularly preferred are graphitised carbons. The Brunauer, Emmett and Teller (BET) surface area of the carbon support material may be between 0 and $2000m^2g^{-1}$, eg between 30 and $400m^2g^{-1}$.

The loading of the precious metal macrocycle compound may be between 0.1 and 70wt% of the carbon support and is preferably between 0.1 and 30wt%.

The loading of the precious metal may be between 0.05 and 20wt% of the carbon support and is preferably between 0.1 and 10wt%.

The invention further provides a method of preparing the carbon supported precursor to the catalytic material comprising dissolving a precious metal macrocyclic compound in aqueous or organic solvent to form a solution, adding carbon to the solution, adsorbing the macrocyclic

material onto the carbon support, and separating the carbon supported macrocyclic material.

Preferably, agitation is employed to aid the adsorption of the macrocyclic material. It is preferably maintained for between 1 and 16 hours. In a method of the invention, it is preferred to dissolve the precious metal macrocyclic compound in sulphuric acid of between 13 and 16 molar concentration to form the solution.

The carbon supported macrocyclic precursor may be prepared by the method according to the invention or by any known method.

The invention further provides a means of activating the precursor materials to produce the catalytic material of the invention, and in which the oxidation state of the metal atom species is changed, comprising the application of a potential to an electrode carrying the carbon supported macrocyclic catalyst precursor, which is immersed in an acid electrolyte, and repeatedly cycling this potential between defined limits for a defined number of cycles.

An electrode bearing the macrocyclic precursor material can be prepared in the conventional manner. This generally involves dispersing the material in a suspension of a hydrophobic material, such as polytetrafluoroethylene (PTFE), coating a substrate such as PTFE wet-proofed graphite paper or carbon cloth with the dispersion and sintering the coated substrate, in either an oxygen-containing atmosphere such as air, or an inert atmosphere such as nitrogen.

In a method of the invention, it is preferred to activate the electrodes, containing the macrocyclic catalysts, to produce the active material by sweeping an applied potential between 0.05 and 2.0V preferably between 0.5 and 1.2V versus a dynamic hydrogen electrode (DHE) at least ten times, in phosphoric acid at elevated temperatures. However, other methods to activate the macrocyclic precursor material which do not require the fabrication of electrodes, for example, use of slurry or suspension electrochemical cells, immersion in hot concentrated acids with gas purging, and gas phase heat treatment, or treatment in controlled atmosphere or atmospheres may be used.

The catalytic material may be used in a fuel cell as the cathode for oxygen reduction or as the anode for hydrogen oxidation. If the material is used as the anode in a fuel cell the hydrogen fuel may contain a minor proportion of carbon monoxide, for example up to 5 vol%.

Although the material according to the invention has particular application in PAFC and PEMFC, and is described herein in detail with reference to its use in the former, it is clear to us that the materials have uses in other fuel cells or for other applications, such as in electrodes for batteries, or as catalysts for other chemical processes.

The invention will now be particularly described in the following examples, which are to be regarded as illustrative and not limiting. Each of the exemplary catalysts was made into test electrodes following the methods outlined above.

The terms of "activity", "electrochemical metal area (ECA)", "specific activity", and "durability" refer to these properties measured according to the methods contained in the following paragraphs. "Gas diffusion electrodes" used are prepared by mixing the catalyst with PTFE, applying to a wet-proofed graphite paper and sintering as is usually practised in the art. In addition, another type of electrode is used in which the amount of PTFE used is sufficiently low to allow the electrode structure to be fully wetted by the electrolyte at 180°C. This is known as a "flooded electrode" and has been described in the literature by H Kunz and G Gruver (J Electrochemical Soc, 122, 1279, 1975) and P Stonehart and P Ross (Electrochim Acta, 21, 441, 1976).

Activity is a measure of the oxygen reduction ability per unit weight of the catalyst material present, and is often referred to as mass activity. Measurements of over-voltage at various current densities are made in an electrochemical half cell using 100% phosphoric acid electrolyte at 180°C, with oxygen and air as the reactants at atmospheric pressure. The current flow through the test electrode at a series of IR (Internal Resistance) free potentials versus a dynamic hydrogen reference electrode (DHE), is measured, and the mass activity, expressed in terms of milliamps per milligram of either total catalyst material, or just the platinum metal present in the electrode, can be calculated at selected potentials and plotted against the IR-free electrode potential. Both the "gas diffusion" and "flooded" types of electrodes can be used to obtain a measurement of the mass activity. An advantage of using the flooded electrodes is that all the catalyst material present on the electrode is wetted with electrolyte and hence is utilised in the activity measurement.

This enables a better comparison of the activities of different catalyst materials.

With gas diffusion electrodes, a plot of potential against the logarithm of the mass activity shows a linear region known as the "Tafel region", which is dominated purely by catalytic kinetic effects. The value for the gradient, known as the "Tafel slope", is dependent on the nature of the catalyst and the operating conditions and can be defined as "x". With the flooded electrodes it is common to observe two distinct linear regions in the same plot, one at the lower current densities, with the same value of the slope of "x", and the other at higher current densities, which typically have a value of "2x". This is due to a contribution from the resistance to gas transfer to the active catalyst sites in the flooded electrode. The true mass activity measurement at any given potential with the flooded electrodes can be obtained by extrapolation of the kinetically controlled slope, of gradient "x", to the measurement potential.

The "electrochemical metal area (ECA)" is a measure of the exposed surface area of the platinum metal catalyst on the electrodes, and is expressed in terms of $m^2g^{-1}Pt$. The ECA is determined in accordance with the method described by S Gilman, J Electroanal Chem, 7, 382, 1964. This method is based on the use of cyclic voltammetry to deposit and strip off a monolayer coverage of hydrogen on the active catalyst surface at potentials close to hydrogen evolution. The hydrogen adsorption is measured on the fully wetted electrode comprising the electrocatalyst material. The charge associated with hydrogen adsorption is measured and using the relationship $1cm^2Pt = 210\mu C$ (C=Coulomb), the electrochemical area of the catalyst is determined.

It can be seen that one way to increase the mass activity of a catalyst material would be to increase the effective surface area of the catalyst (eg, by reducing the particle size). In this instance this does not necessarily mean that the intrinsic activity of the catalyst surface has changed. The other approach to increasing mass activity is to actually increase the intrinsic activity of the surface. This is known as the "specific activity" and is defined as the oxygen reduction current, as measured above, which is available per unit surface area of the active catalyst metal. It is expressed in terms of μAcm^{-2} of catalyst surface, and is obtained by dividing the mass activity by the electrochemical metal area. This is the fundamental measurement of the catalytic activity of different surfaces.

To assess the longer term durability of the catalyst material under more realistic fuel cell operating conditions, an accelerated "durability" test has been developed. It is again advantageous to use the flooded gas diffusion electrodes since effects on performance due to variations in the electrode structure and the degree of electrolyte wetting can be eliminated, and only performance changes due to the stability properties of the catalyst are observed. The durability measurement is made by applying a galvanostatic load (ie a fixed current density) to the electrode, with pure oxygen as a reactant, in 100% phosphoric acid at 180°C, and recording the electrode voltage change with time. These operating conditions are more severe than those employed in practical fuel cell operation, and as such this test provides relevant information on catalyst durability over a shorter time period than the actual design lifetime of a fuel cell system.

I. Activity of Electrodes for Oxygen Reduction Reaction

EXAMPLE 1

Platinum Catalyst Derived from Platinum Phthalocyanine

The method of preparation used was a precipitation method as described in GB 2164785A. A platinum phthalocyanine precursor to the catalytic material, having 0.87% by weight of platinum, was prepared by dissolving platinum phthalocyanine (0.068g) in 18.4M sulphuric acid (25cm^3) at room temperature. The solution was stirred, and graphitised Shawinigan carbon (2.0g), an acetylene black carbon of BET surface area 55m^{2}g^{-1}, (the ungraphitised Shawinigan is available from Chevron Chemicals, Houston, Texas, USA) was added to form a viscous slurry which was stirred for 15 minutes. Stirring was continued for approximately 30 minutes while water (30cm^3) was added dropwise and the slurry cooled by an ice bath. Cooling was continued for a further hour at room temperature. The slurry was then filtered and washed with water until the pH of the supernatant liquid was pH6. The resultant filtered catalytic material precursor was dried at 105°C.

Hydrophobic gas diffusion electrodes with 30wt% PTFE were prepared from this macrocyclic catalyst precursor material, using conventional methods as described above. The electrode preparation was completed by heat treatment in air at 350°C for 15 minutes. The electrode was activated prior to making activity measurements by placing the electrode in the electrochemical half cell, and sweeping an applied potential between 0.05 and 1.20V versus the DHE reference at least ten

times, under conditions of 100% phosphoric acid electrolyte at 180°C, with air passing down the gas side of the electrode sample.

EXAMPLE 2

Iridium Catalyst Derived from Iridium Phthalocyanine

The method described in Example 1 was used to produce a 3.5% iridium phthalocyanine precursor to the catalytic material, having 0.62wt% Ir. The electrode was activated as described in Example 1 to produce the active catalytic material.

EXAMPLE 3

Platinum Catalyst Derived from Platinum Phthalocyanine

A platinum phthalocyanine precursor to the catalytic material was prepared according to the method of the invention. Platinum phthalocyanine (0.064g) was dissolved in 14M sulphuric acid (50cm^3). Dried graphitised Shawinigan carbon, (2.0g) was added to the solution to produce a slurry which was kept at room temperature and stirred for 16 hours. The slurry was filtered and washed with 14M sulphuric acid (50cm^3) and then demineralised water until the supernatant liquid was pH 5.5-6. The method of preparation was an adsorption method, and the catalyst assayed (by Emission Spectroscopy) as 0.64wt% Pt.

Gas diffusion electrodes were prepared and the activation procedure was carried out as described in Example 1 above.

EXAMPLE 4

Iridium Catalyst Derived from Iridium Phthalocyanine

The method described in Example 3 was used to produce a carbon supported iridium phthalocyanine material, with a loading of 0.22wt% Ir. The catalyst was activated as described in Example 1.

Examples 1, 2, 3 and 4 were tested as described above for their activity for oxygen reduction with 100% phosphoric acid as the electrolyte at 180°C. The polarisation curves of voltage versus current density in terms of $mAmg^{-1}$ (platinum group metal) obtained are shown in Figure 1.

Measured values for the mass activity of Examples 1, 2, 3 and 4 with respect to oxygen reduction, versus DHE, and with an electrolyte of 100% phosphoric acid at 180°C are given in Table 1 below.

TABLE 1

Example	Catalyst Precursor	Assay (wt% metal)	Mass Activity ($mAmg^{-1}$ precursor, at 850mV)	($mAmg^{-1}$ metal, at 900mV)
1	Platinum Phthalocyanine	0.87% Pt	9.5	12.0
2	Iridium Phthalocyanine	0.62% Ir	11.5	16.0
3	Platinum Phthalocyanine	0.64% Pt	13.0	16.0
4	Iridium Phthalocyanine	0.22% Ir	14.6	46.0

The results in Table 1 above show that the activity, in terms of $mAmg^{-1}$ of macrocycle catalyst precursor at 850mV, are superior to the

activity of all prior art macrocycle-based catalyst evaluated in acid electrolytes. Furthermore, the catalysts prepared by the method of the invention, Examples 3 and 4, are superior to the catalysts of Examples 1 and 2, prepared by the precipitation method, which is commonly practised in the art.

EXAMPLE 5

Platinum Catalyst Derived from Platinum Phthalocyanine

A further example of the novel catalyst material that is the subject of the invention was produced according to the methods disclosed in this invention. Platinum phthalocyanine (1.234g) was dissolved in 14M sulphuric acid (1000cm³). Dried, graphitised Ketjenblack EC300J carbon (4.0g), (the ungraphitised Ketjenblack is available from Akzo Chemie Nederland bv, Amersfoort, Netherlands) having a BET surface area of $252m^2 g^{-1}$, was added to the solution to produce a slurry which was kept at room temperature and stirred for 16 hours. The slurry was filtered and washed with 14M sulphuric acid (50cm³) and then demineralised water until the supernatant liquid was pH 5.5-6.0. The material so produced was dried in air at 105°C. The method of preparation was an adsorption method, and the catalyst precursor assayed at 4.7wt% Pt.

A "flooded" type of electrode was fabricated using the platinum phthalocyanine material, as described above, by using 10% PTFE content in the electrode rather than the higher quantities normally employed in the fabrication of gas diffusion electrodes. In addition, the electrode preparation was completed by sintering in nitrogen at 330°C.

A number of electrodes of the above type were activated in 100% phosphoric acid, at 180°C, by sweeping the potential between 0.05V and a range of values from 1.05 and 1.35V (versus DHE) at a rate of 30mVs-1 for a period of 930 minutes with nitrogen gas flowing past the gas side of the electrode. The measurements of current density and over-voltage were then carried out using oxygen as the reactant gas.

The effect of the differing higher potential limits on the activity displayed by the catalyst material is shown in Figure 2. It can clearly be seen from the data that sweeping to an increasingly higher positive potential increases the mass activity of the resultant active catalyst material. Also shown in Figure 2 is the activity of an electrode comprising the precursor material, measured prior to the carrying out of the activation step of cycling the potential between 0.05V and a high positive potential. This shows that the precursor material, which comprises platinum phthalocyanine, with platinum in the +2 oxidation state, possesses very low activity for oxygen reduction.

EXAMPLE 6

Platinum Catalyst Derived from Platinum Tetraazaannulene

A further example of the novel catalyst material that is the subject of the invention was produced, according to the methods disclosed in this invention, using a tetraazaannulene macrocyclic precursor. [Dibenzo[b,i]1,4,8,11-tetraazacyclotetradecinato]platinum(II), (PtTADA), (0.06g) was dissolved in 14M sulphuric acid (150cm^3). Dried graphitised Shawinigan acetylene black carbon (1.0g), was added to the solution to produce a slurry which was kept at room temperature and stirred for

16 hours. The slurry was filtered and washed with 14M sulphuric acid (50cm^3) and then demineralised water until the supernatant liquid was pH 5.5-6.0. The material so produced was dried in air at 105°C. The method of preparation was an adsorption one, and the catalyst precursor assayed at 2.2wt% Pt. A gas diffusion electrode was prepared using 30wt% PTFE followed by sintering in air at 350°C. The electrode was then activated as described above, by sweeping to an upper potential of 1.20V versus DHE, for 1000 minutes, with a flow of nitrogen down the gas side of the test electrode. Although fabricated as a gas diffusion electrode, the electrochemical measurements indicated that the structure had fully flooded during the activation and as a result demonstrated flooded electrode type behaviour.

COMPARATIVE EXAMPLE A

Platinum Catalyst Prepared by Conventional Method

A conventional platinum catalyst material, as presently used in fuel cells, was prepared by adding Shawinigan acetylene black carbon (450g) to water (70 litres) at 60°C over 5 minutes to produce a slurry. Sodium bicarbonate (116.5g) in water (700cm^3) was added to the slurry which was stirred for 5 minutes before heating to 100°C for 30 minutes. A solution of platinum (50g) as chloroplatinic acid in water (2000cm^3) was added to the slurry over 12 minutes. The slurry was boiled for 2 hours, and cooled to 90°C. A 1% formaldehyde solution (1400cm^3) was added, and the slurry boiled for a further 1 hour, after which it was filtered and washed free of soluble chloride ions with water. The platinum catalyst material so-produced was then dried at 105°C. The catalyst had an assay of 9.73wt% Pt.

COMPARATIVE EXAMPLE B

Platinum/Nickel Alloy Catalyst

A state of the art alloy catalyst comprising platinum and
nickel was prepared at 10wt% Pt loading according to the method
described in US 5,068,161. Shawinigan acetylene black (44.1g) was
added to demineralised water (2000cm³) and stirred for 15 minutes to
produce a homogeneous slurry. Sodium bicarbonate (15.49g) was added
to the slurry and stirred for 5 minutes. The temperature of the slurry
was raised to 100°C and maintained at the boil for 30 minutes. A
solution of platinum (5.0g) as chloroplatinic acid, in demineralised water
(60cm³), was added subsurface to the slurry over 5 minutes. The slurry
was boiled for 5 minutes. A solution of nickel (0.9g) as the nitrate salt
(Ni(NO₃)₂.6H₂O, 4.46g), in demineralised water (50cm³) was added over
10 minutes. The slurry was boiled for a further 2 hours. Formaldehyde
solution (3.9cm³), diluted to 39cm³ was added over 10 minutes. The
slurry was boiled for a further 60 minutes and then filtered to remove
supernatant liquid and washed with demineralised water to remove soluble
chloride species. The chloride-free filter cake was vacuum dried at 80°C
until the moisture content was less than 2%. The material was then
heated to a temperature of 930°C in a flowing nitrogen atmosphere and
maintained at this temperature for 60 minutes to form the alloy. This
gave a catalyst of 9.69wt% Pt, 1.65wt% Ni and a Pt:Ni atomic ratio of
64:36.

Flooded electrodes of Comparative Examples A and B and Example 5 were fabricated, as described above. Example 5 was activated as described above, sweeping to a potential of 1.32V versus DHE. The electrodes of Examples 5 and 6 and Comparative Examples A and B were evaluated for oxygen reduction activity in 100% phosphoric acid, at 180°C. Mass activities were calculated using the Pt assays of the electrodes after testing to account for any metal lost during the test. The polarisation curves of voltage versus mass activity obtained are shown in Figure 3.

As described above, flooded-type electrodes show polarisation curves that have two linear portions when voltage is plotted against the logarithm of the current density (or mass activity). Extrapolation of the lower current linear slopes, to a selected measurement potential of 900mV, allows direct comparison of different catalyst types in terms of mass or specific activity. The extrapolation results are shown in Table 2.

TABLE 2

Example	Mass Activity
	$(mAmg^{-1}$ Pt at 900mV)
Comparative Example A	(Pt) 33
Comparative Example B	(Pt/Ni) 53
Example 5	(PtPc) 103
Example 6	(PtTADA) 75

As can be seen from the data in Table 2, extrapolated mass activities for Comparative Examples A and B agree well with those values

described above for conventional state of the art carbon supported pure platinum and platinum/base metal alloy catalysts.

The results as shown in Figure 3 and Table 2, show that the catalyst of the invention are significantly superior in mass activity to conventional state of the art platinum group metal catalysts.

II. DURABILITY OF ELECTRODES TO POTENTIAL LOSS DURING OXYGEN REDUCTION

Comparative Examples A and B and Example 5 fabricated into flooded-type electrodes were tested for durability with oxygen as the reactant in 100% phosphoric acid at 180°C under galvanostatic (constant current density, ie load) control for 6 hours. The electrode of Example 5 was activated in 100% phosphoric acid, at 180°C, by sweeping the potential between 0.05 and 1.05V (versus DHE) at a rate of $30mVs^{-1}$ for a period of 930 minutes with nitrogen gas flowing past the gas side of the electrode. In each case, in the galvanostatic test, the load was set to achieve an initial potential of 850-800mV vs DHE. It is known that catalyst de-activation is very highly dependent on applied operating potential, and current density has a comparatively smaller effect.

After 6 hours at a load of $50mAcm^{-2}$, Comparative Example A experienced a drop in potential of 130mV, whereas, under a similar load, Comparative Example B experienced a drop in potential of 105mV. Example 5, under load of $3.7mAcm^{-2}$ experienced a potential drop of only 20mV during the 6 hour period.

The results are shown in Figure 4. This data clearly demonstrates that the catalyst materials of the invention possess far greater resistance to catalyst de-activation when compared to the currently used catalyst materials.

III. NATURE OF THE ELECTROCATALYTIC MATERIAL

The physical nature of the active material of Example 5 was investigated using X-ray Photoelectron Spectroscopy (XPS) and cyclic voltammetry, both of which are commonly used by workers in this field to characterise the surfaces of catalytic materials.

The XPS of Example 5 as the macrocyclic precursor to the active catalyst and as a tested electrode after activation to produce the active catalyst of this invention showed the change in the oxidation state of platinum (Table 3 and Figure 5).

TABLE 3

Sample	$Pt4f_{7/2}$ Binding Energy
Platinum phthalocyanine macrocyclic precursor	73.6
Electrode of "activated" Pt catalyst	71.5

The shift in the platinum binding energy from 73.6 to 71.5eV on use as an oxygen reduction catalyst represents a change in platinum oxidation state from (+2) to (0). This shows that the active catalytic material in Example 5 has platinum in the (0) oxidation state.

Cyclic voltammetry is a technique used with conventional platinum catalysts to determine active catalyst metal areas. The ECA measurement, as described above, gives an indication of exposed surface area of platinum metal in the (0) oxidation state. The cyclic voltammogram of platinum (0) has a unique and characteristic signal in the potential range 0-0.3V (versus DHE) which is ascribed to the formation of a monolayer coverage of adsorbed hydrogen on the platinum (0) surface. The amount of hydrogen adsorbed can be measured and is directly related to the platinum (0) surface area. Figure 6 shows the cyclic voltammetry of Comparative Example A and Example 5 after use as oxygen reduction catalysts respectively. Table 4 shows the ECA calculated from each voltammogram.

TABLE 4

Example	ECA $(m^2 g^{-1} Pt)$	Specific Activity $(\mu A cm^{-2} Pt)$
Comparative Example A	50	58
Example 5	17	604

It is clear from these voltammograms that although the catalyst material of the invention comprises platinum in the (0) oxidation state, it does not adsorb hydrogen in the same manner as conventional platinum (0) catalysts. The cyclic voltammetry shows that the catalyst of Example 5 adsorbs much less hydrogen compared to Comparative Example A. However, as shown above, the mass activity demonstrated by the catalyst of Example 5 is the superior.

When the mass activity values from Table 2 and the ECA data are used to determine the specific activity of the surfaces, the values as shown in Table 4 are obtained.

5   Conventional carbon-supported platinum catalyst have specific activities in the range $30\text{-}60\mu Acm^{-2}$, as is commonly reported in the prior art, (see for example, L J Bregoli in Electrochim Acta, 23, 489 (1978)). Comparative Example A shows a specific activity which lies in this range. However, Example 5 demonstrates a much higher specific activity than has

10   previously reported for any platinum or platinum-based catalyst system. Indeed, by varying the positive potential of the activation sweep between 1.05 and 1.35V (versus DHE), specific activities in the range of $200\text{-}600\mu Acm^{-2}$ have been measured.

15   Whatever the explanation for these unexpected results, the materials of the invention are a form of platinum in the zero oxidation state, which show significantly different properties from platinum (0) prepared by conventional methods, as demonstrated above, and which in particular can be characterised by their greater mass activity and enhanced

20   stability under fuel cell operating conditions, compared to state of the art materials, which will lead to benefits of higher output performance and longer operational life.

<u>CLAIMS</u>　　（82年3月修正）

1.　　　A catalyst material derived from precious metal-containing macrocyclic compound precursors and as a carbon support supported on high surface area carbon of BET surface area 0–2000m^{2}g^{-1}, wherein the catalyst material contains precious metal selected from the group platinum, palladium, ruthenium, osmium, rhodium, iridium, silver and gold, in zero oxidation state.

2.　　　A catalyst material according to claim 1 wherein said catalyst material is the product of an activation process on the precursor.

3.　　　A catalyst material according to claim 1 wherein the precious metal is platinum or iridium.

4.　　　A catalyst material according to claim 1 wherein the macrocycle in the macrocyclic compound is an N4-chelate compound.

5.　　　A catalyst material according to claim 4 wherein the macrocycle is a phthalocyanine or tetraazaannulene.

6.　　　A catalyst material according to claim 1 or claim 5 wherein the high surface area carbon is a conductive graphitised carbon.

7.　　　A catalyst material according to claim 1 wherein the carbon has a BET surface area of 30-400 m^{2}g^{-1}.

8.   A catalyst material according to claim 1 wherein the loading of the precious metal is 0.05 to 20 wt% of the carbon support.

9.   A catalyst material according to claim 8 wherein the loading of the precious metal is 0.1 to 10 wt% of the carbon support.

10.   A catalyst material derived from precious metal-containing macrocyclic compound precursors in which the macrocyclic compound is an N4-chelate compound, and supported on a high surface area carbon which is a conductive graphitised carbon, of BET surface area $0\text{-}2000\text{m}^2\text{g}^{-1}$, wherein the catalyst material contains precious metal selected from the group platinum, palladium, ruthenium, osmium, iridium, rhodium, silver and gold, in a loading of 0.05-20wt% of the carbon support, in 300 oxidation state.

11.   A fuel cell wherein at least one electrode is coated with a catalyst material according to claim 1 or claim 10.

12.   An electrode wherein said electrode is coated with a catalyst material according to claim 1 or claim 10.

13.   A method for the preparation of a carbon-supported precious metal-containing macrocyclic compound precursor to a catalyst material according to claim 1 or claim 10, comprising dissolving a precious metal macrocyclic compound in aqueous or organic solvent to form a solution, adding conductive carbon to the solution, absorbing the macrocyclic material onto the carbon support, and separating the carbon-supported macrocyclic material.

14.   A method according to claim 13 wherein the solution is agitated for 1-16 hours after addition of the carbon.

15.   A method for the activation of a carbon-supported precious metal-containing macrocyclic compound precursor to a catalyst material according to claim 1 or claim 10, which activation effects a change in the oxidation state of the metal, comprising repeatedly sweeping an applied potential to an electrode carrying the carbon-supported macrocyclic compound precursor which is immersed in an acid electrolyte.

16.   A method according to claim 15 wherein the applied potential is 0.05-2.0V.

CATALYST MATERIAL DERIVED FROM PRECIOUS METAL-
CONTAINING MACROCYCLIC COMPOUND PRECURSORS, THE
METHOD FOR PREPARATION THEREOF AND THE METHOD
FOR ACTIVATING THE CARBON-SUPPORTED PRECIOUS METAL

Abstract of the Invention

5   An improved catalyst material is derived from a precious
metal-containing macrocyclic compound precursor, which contains precious
metal in zero oxidation state.   The material may be produced by
activating the compound, for example by a voltage sweep.   The material
offers useful improvements in activity and resistance to de-activation, when
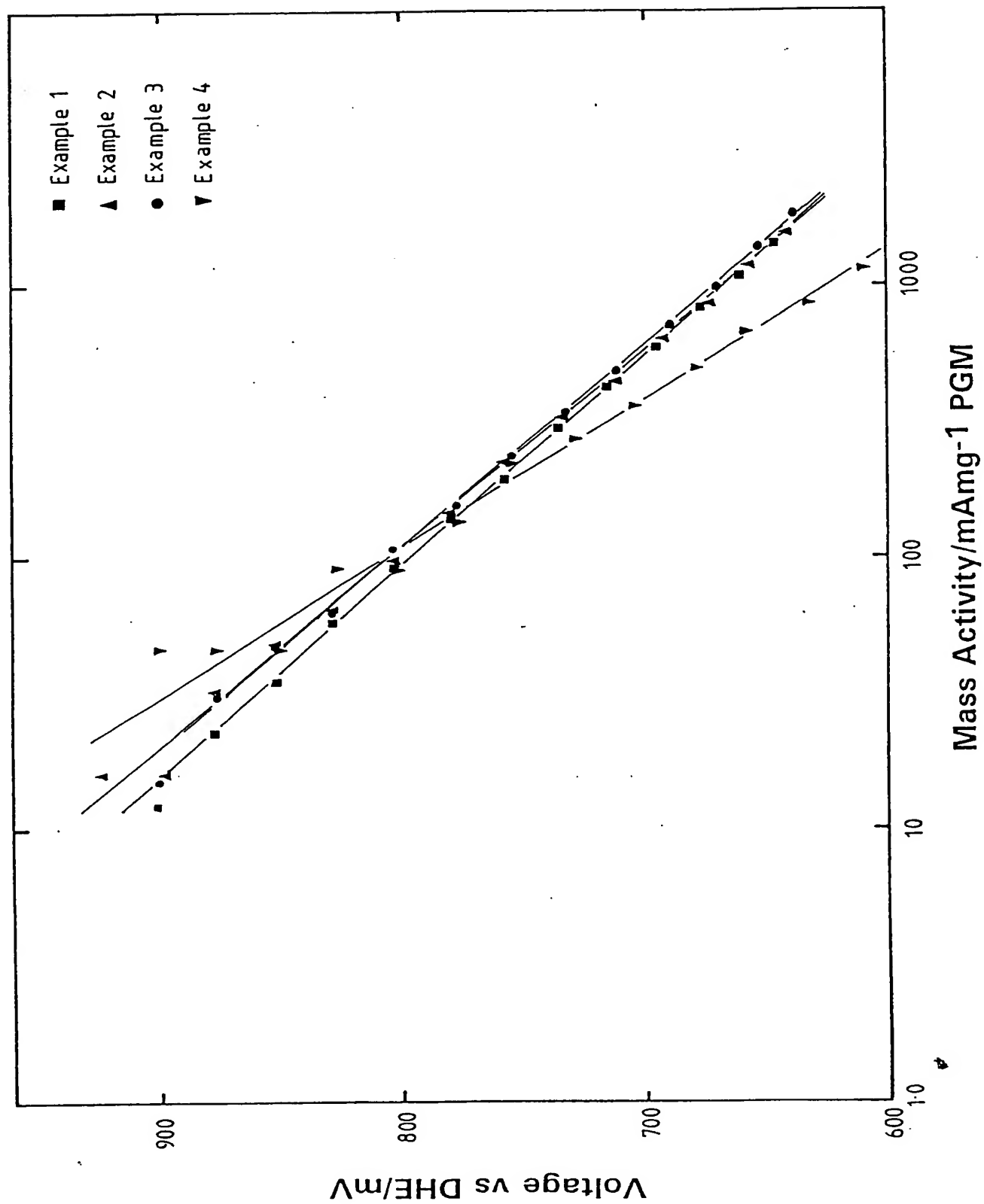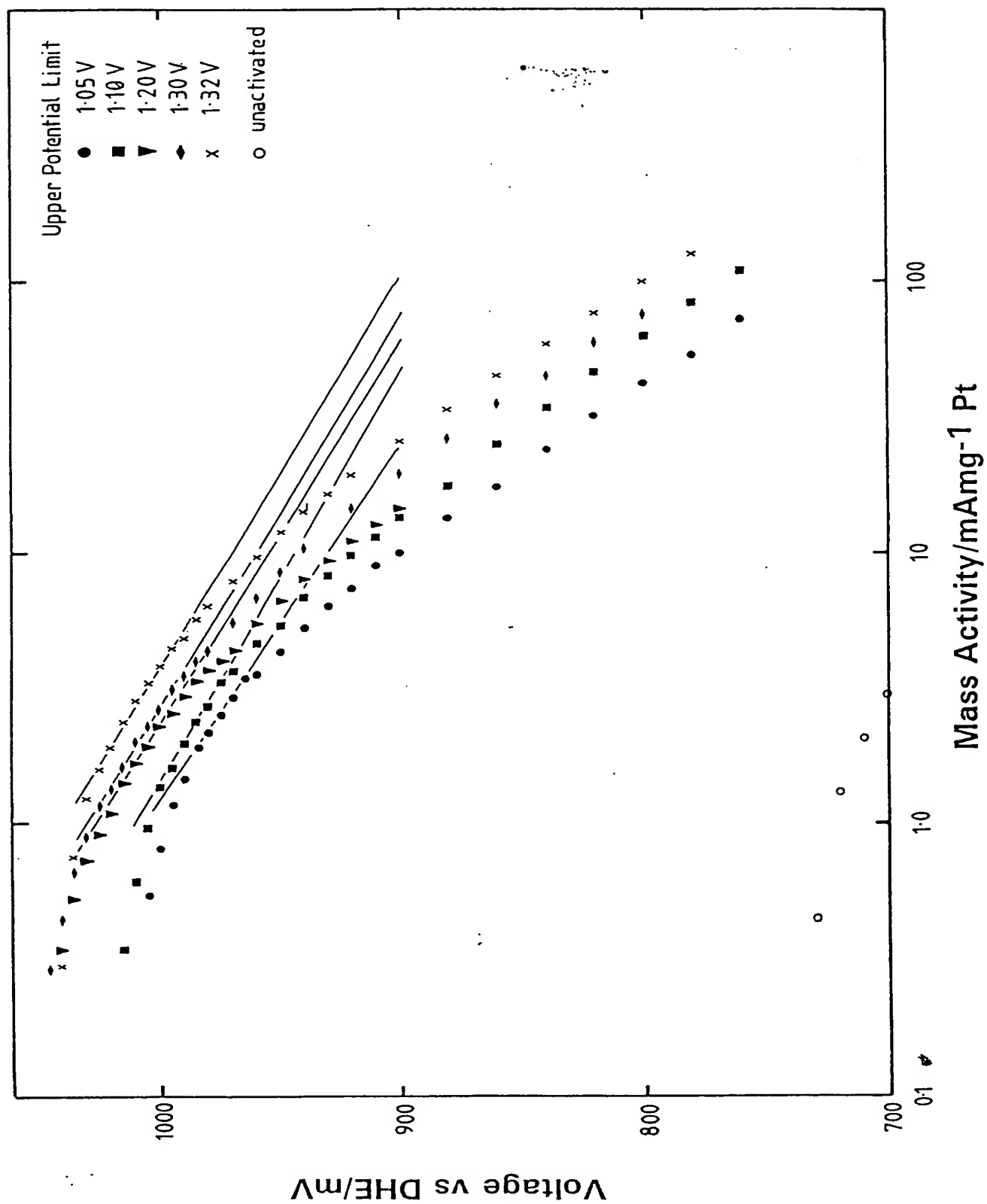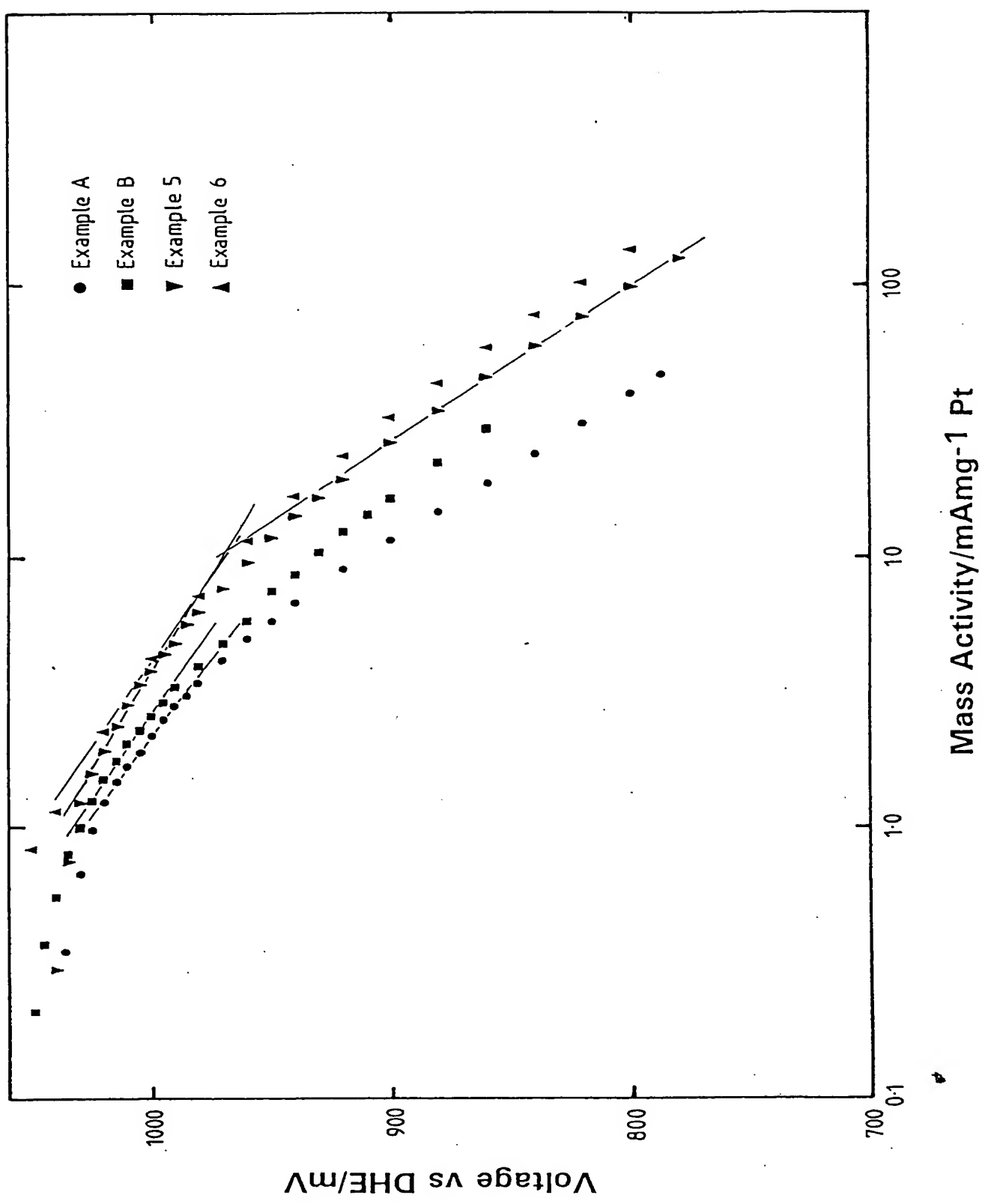10   used as a fuel cell catalyst.

FIGURE 1

Mass Activity/mAmg⁻¹ PGM

Voltage vs DHE/mV

- Example 1
- Example 2
- Example 3
- Example 4

FIGURE 2

FIGURE 3

Voltage vs DHE/mV

Mass Activity/mAmg⁻¹ Pt

- Example A
- Example B
- Example 5
- Example 6

1000 900 800 700

0·1 1·0 10 100

FIGURE 4

FIGURE 5

Example 5 before activation
Example 5 after use

Binding Energy/eV

Intensity

FIGURE 6

Example A

Example 5

Current/mA

Voltage vs RHE/V